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A molecular dynamics study of the atomic structure of $(\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}$ glass with $x = 0.625$ close to the eutectic

B W M Thomas, R N Mead and G Mountjoy¹

School of Physical Sciences, University of Kent, Canterbury CT2 7NR, UK

E-mail: g.mountjoy@kent.ac.uk and mountjoy@unica.it

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Abstract

Aluminate glasses are difficult to prepare as they do not contain traditional network formers, but they are promising materials for optical applications. The atomic structure of calcium aluminate glasses has been studied using several experimental techniques. The current study uses molecular dynamics to obtain a model of a $(\text{CaO})_{0.625}(\text{Al}_2\text{O}_3)_{0.375}$ glass close to the eutectic. The glass consists of a tetrahedral alumina network with average network polymerization $\langle Q^n \rangle$ of $n = 3.3$. Ca acts as a network modifier with average coordination of 6.2. Ca is typically coordinated to three bridging oxygens (O_b) and three non-bridging oxygens (O_{nb}), with Ca– O_{nb} bonds noticeably shorter than the Ca– O_b bonds. A new method of analysing modifier cation coordination is presented, which specifically shows the distribution of Ca coordination N_{CaO} in terms of combinations of N_{CaO_b} and $N_{\text{CaO}_{nb}}$. O_b is most often coordinated to two Al plus two Ca, and O_{nb} is most often coordinated to one Al plus three Ca. The typical coordinations of Ca, O_b , and O_{nb} all have a noticeable similarity to those for the $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ crystal. The Ca–Ca distribution shows a clear similarity to that for $(\text{CaO})_{0.5}(\text{SiO}_2)_{0.5}$ glass, and this is attributed to the equal atomic number densities of Ca in these glasses.

1. Introduction

Studies of aluminate glasses have been motivated by their promising optical properties, such as ultralow optical losses [1], and wide optical transmission window extending to infrared wavelengths of $\sim 5 \mu\text{m}$ [2]. Both are due to the low vibrational frequencies in aluminate glasses in comparison to silicate glasses. Unfortunately, these favourable optical properties

¹ Author to whom any correspondence should be addressed. Present address: Dipartimento di Scienze Chimiche, Università di Cagliari, Complesso Universitario, S.S. 554 bivio per Sestu, 09042 Monserrato (Cagliari), Italy.

are combined with limited glass forming ability, and the addition of traditional network formers such as Si would be counterproductive for optical applications. Recently developed containerless methods [3], using aerodynamic levitation, have facilitated the study of aluminate glasses, because they eliminate crystallization induced by a container in contact with the glass surface.

Aluminate glasses are unusual because they do not contain one of the traditional oxide glass formers, e.g. B, Si or P. Although Al is frequently an additive in oxide glasses, where it takes the role of a network former, it is found that aluminate glasses themselves are not easy glass formers. The most frequently reported binary aluminate glasses are calcium aluminate glasses, $(\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}$. This binary system has a eutectic at approximately $x \sim 0.6$, in the vicinity of two $n\text{CaO}\cdot m\text{Al}_2\text{O}_3$ crystals with $n:m$ ratios of 5:3 ($x = 0.625$) and 12:7 ($x = 0.632$). $(\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}$ glasses have been prepared with $x \sim 0.6$ by normal melt quenching, and with x from ~ 0.5 to ~ 0.7 by rapid melt quenching (e.g. splat cooling) or containerless methods.

There have been a few previous experimental studies of the structure of $(\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}$ glasses. These have included infrared [4] and Raman [5] spectroscopy, ^{17}O [6] and ^{27}Al [7] NMR spectroscopy, and x-ray [8, 9] and neutron diffraction [9, 10]. Glasses of composition $x \sim 0.63$ have been studied by all of these techniques. Experimental results for glasses with $x \geq 0.5$, including neutron diffraction results for a glass with $x = 0.62$ [10], indicate a tetrahedral alumina network. However, neutron diffraction results for a glass with $x = 0.64$ showed a mixture of fourfold- and fivefold-coordinated Al [9]. Studies of $(\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}$ liquids [11, 12] using NMR spectroscopy, diffraction, and ion simulation, indicate that the average Al–O coordination is higher in the liquid than the glass. These observations indicate that the fabrication method (e.g. splat cooling versus containerless) is likely to influence the final glass structure. The Ca coordination could not be determined from neutron diffraction data [9, 10].

A modelling study of $(\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}$ glass can provide a valuable complement to experimental results for further developing concepts of the atomic structure. There have been no previously reported modelling studies devoted to $(\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}$ glasses². However, a previous study of calcium aluminosilicate glasses [13] included results for a glass with zero silica content, i.e. $(\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}$, which had $x = 0.61$. The current study presents a detailed model of the atomic structure of a $(\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}$ glass, with the composition $x = 0.625$ chosen to be close to the eutectic, and to be suitable for comparison with the widest range of experimental data. The model is obtained using molecular dynamics, and then compared with experimental results. The model is also compared in detail with $n\text{CaO}\cdot m\text{Al}_2\text{O}_3$ crystals and with $(\text{CaO})_x(\text{SiO}_2)_{1-x}$ glasses. This reveals key features of the atomic structure of the glass, including local atomic environments of Al, Ca, and O.

2. Molecular dynamics method

Interatomic potentials for $(\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}$ were obtained from the literature. Four different potentials were evaluated [13–16]. All of these used two-body interactions of the form

$$V_{ij}(r) = \frac{q_i q_j}{4\pi \epsilon_0 r_{ij}} + A_{ij} \exp\left(\frac{-r_{ij}}{\rho}\right) - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

where $V_{ij}(r)$ is the potential, i and j are element types, r is distance, q is charge, and A , ρ , and C are potential parameters. (One potential [13] included an additional two-body term

² The authors have just learned of a new modelling study: Kang E T, Lee S J and Hannon A C 2006 *J. Non-Cryst. Solids* at press.

Table 1. Potential parameters used in this study [16].

$i-j$	q_i (e)	A_{ij} (eV)	ρ_{ij} (Å)	C_{ij} (eV Å ⁻⁶)
Al–O	1.8	12 201	0.1956	31.99
Ca–O	1.2	7 747	0.2526	93.10
O–O	–1.2	1 844	0.3436	192.5

Table 2. Comparison of crystal structures (see the text for references) from experiment (roman text) and modelling (italic text). (Note that 12C7A was not modelled as it contains overlapping partially occupied oxygen sites.)

Structural parameter	CaO lime	Al ₂ O ₃ corundum	CA2	CA	C5A3	C12A7	C3A
a (Å)	4.811 <i>4.773</i>	4.760 <i>4.768</i>	12.839 <i>12.790</i>	8.700 <i>8.735</i>	11.253 <i>11.2950</i>	11.989	15.263 <i>15.213</i>
b (Å)	4.811 <i>4.773</i>	4.760 <i>4.768</i>	8.862 <i>8.904</i>	8.092 <i>8.018</i>	10.966 <i>11.116</i>	11.989	15.263 <i>15.213</i>
c (Å)	4.811 <i>4.773</i>	12.993 <i>13.164</i>	5.431 <i>5.500</i>	15.191 <i>15.334</i>	10.290 <i>10.293</i>	11.989	15.263 <i>15.213</i>
$R_{\text{Al–O}}$ (Å)		1.913 <i>1.925</i>	1.755 <i>1.760</i>	1.753 <i>1.750</i>	1.762 <i>1.749</i>	1.742	1.752 <i>1.742</i>
$R_{\text{Ca–O}}$ (Å)	2.405 <i>2.386</i>		2.527 <i>2.587</i>	2.495 <i>2.535</i>	2.416 <i>2.480</i>	2.417	2.505 <i>2.516</i>
O–Al–O (deg)		109.4 <i>109.3</i>	109.3 <i>109.3</i>	109.3 <i>109.3</i>	109.2 <i>109.3</i>	109.2	109.4 <i>109.3</i>
Al–O–Al (deg)		89.4, 164.2 <i>89.5, 165.0</i>	124.2 <i>124.7</i>	122.4 <i>123.5</i>	123.7 <i>128.3</i>	137.5	152.3 <i>162.5</i>
O–Ca–O (deg)	90.0, 180.0		74.1, 112.5, 143.7	80.4, 123.1, 171.8	83.3, 138.1	80.2, 121.7, 155.2	81.4, 115.3, 173.8
	<i>90.0,</i> <i>180.0</i>		<i>90.3,</i> <i>120.0,</i> <i>158.1</i>	<i>82.3,</i> <i>119.2,</i> <i>172.7</i>	<i>83.6,</i> <i>138.6</i>		<i>81.0,</i> <i>119.0,</i> <i>166.7</i>
B (GPa)	111 <i>117</i>	257 <i>268</i>			<i>110</i>		<i>106</i>

in r^{-8} for Ca–O and a three-body term for O–Al–O.) The potentials were evaluated by using the GULP program [17] to model crystals of CaO (lime) [18] and Al₂O₃ (corundum) [19], and $n\text{CaO}\cdot m\text{Al}_2\text{O}_3$ crystals with $n:m$ ratios of 1:2 [20], 1:1 [21], 5:3 [22], 12:7 [23], and 3:1 [24] (the crystal data were obtained from CDS, UK [25]). The potential from Teter [16] was selected because it gave more accurate average values of $R_{\text{Al–O}}$ and $R_{\text{Ca–O}}$, and O–Al–O, Al–O–Al, and O–Ca–O bond angles. In addition, it gave significantly more accurate values of the bulk modulus, B . The potential parameters are shown in table 1, and a comparison between experimental and modelled crystal structures is shown in table 2.

Molecular dynamics (MD) was used to obtain a model of the atomic structure of $(\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}$ glass with composition $x = 0.625$ (corresponding to the composition $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$). This composition was chosen to give a round number of atoms, to be close to the eutectic, and to be suitable for comparison with the widest range of experimental data, including neutron and x-ray diffraction data for compositions $x = 0.62$ [10], 0.632 [8], and

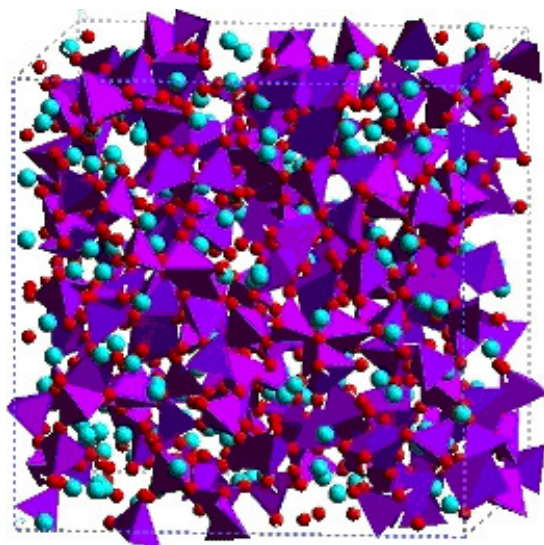


Figure 1. Image of the model of $(\text{CaO})_{0.625}(\text{Al}_2\text{O}_3)_{0.375}$ glass (light spheres are Ca, dark spheres are O, and tetrahedra are AlO_4 groups).[-22pt]

(This figure is in colour only in the electronic version)

0.64 [9]. The reported experimental densities were 2.907 , 2.92 , and 2.90 g cm^{-3} (respectively), and for the model a density of 2.92 g cm^{-3} was specified (as discussed below). The model has a total of 1000 atoms (240 Al, 200 Ca, and 560 O) in a cubic box with length 23.7 \AA . A random starting configuration and periodic boundary conditions were used. The Coulomb potential was evaluated using the Ewald sum method with a precision of 10^{-5} , and the non-Coulomb potential was evaluated using a short range cut-off of 10 \AA .

The MD modelling used the DLPOLY program [26], with time steps of 2 fs, and with a Berendsen NVT thermostat, with a relaxation time of 2 ps. A Berendsen NVT thermostat (i.e. constant volume) was used to obtain a final density compatible with the experimental results. As a consequence, the model obtained has a negative pressure (a model with atmospheric pressure would have a density 3% higher than the experimental density). The modelling used five stages: temperature baths at 6000, 4000, and 2000 K, with 40 000 time steps, and a temperature quench from 2000 to 300 K with 85 000 time steps. During these five stages equilibration was used to keep the temperature constant, and during the first four stages thermal expansion coefficients of 1.03, 1.015, 1.005 were used. A trajectory of 40 000 time steps was used as this enabled atoms to diffuse over half the box length at 6000 K. The quench rate during modelling was 10^{13} K s^{-1} , which is typical for MD studies of glasses, e.g. [13, 16, 27]. Due to constraints on computing time, all MD studies of glasses use quench rates which are several orders of magnitude higher than in experiments. Despite this (the general role of quench rates is under ongoing investigation, e.g. in [28]), MD studies have been able to provide key insights into glass structures. A final stage consisted of use of a temperature bath at 300 K without equilibration, with 40 000 time steps, during which the temperature remained constant and structural parameters were sampled (every 200 time steps).

3. Results

Figure 1 shows an image of the model of $(\text{CaO})_{0.625}(\text{Al}_2\text{O}_3)_{0.375}$ glass. Visual inspection indicates there is a tetrahedral alumina network. Figure 2 shows the partial radial distribution

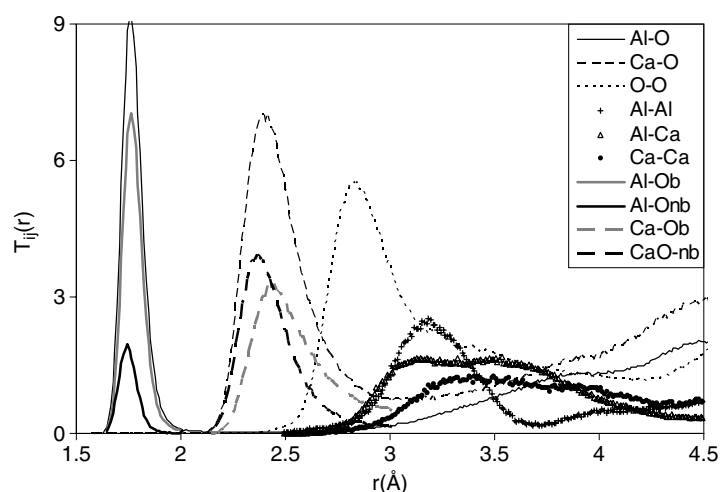


Figure 2. Radial distribution functions $T_{ij}(r)$ for the model of $(\text{CaO})_{0.625}(\text{Al}_2\text{O}_3)_{0.375}$ glass, including the distinction between bridging (O_b) and non-bridging (O_{nb}) oxygens. (Note that the Al–O correlations have been scaled $\frac{1}{2} \times$.)

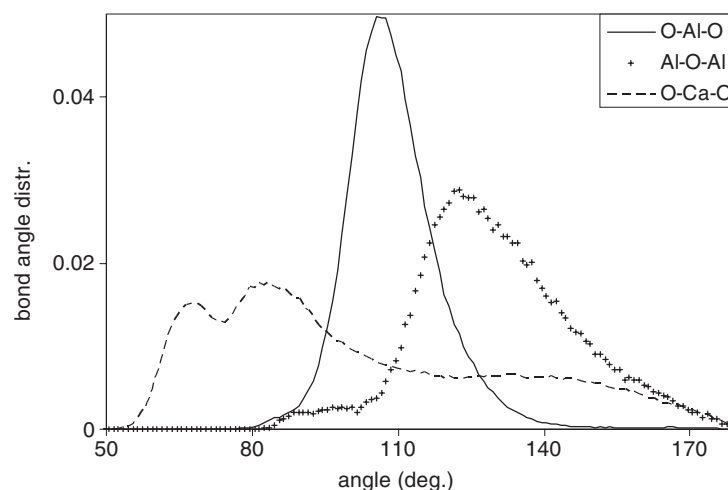


Figure 3. Bond angle distributions for the model of $(\text{CaO})_{0.625}(\text{Al}_2\text{O}_3)_{0.375}$ glass.

functions $T_{ij}(r)$ for the model, where

$$T_{ij}(r) = \frac{1}{r} \left(\frac{1}{N_i} \sum_{i=1}^{N_i} \sum_{j \neq i}^N \delta(r - R_{ij}) \right) \quad (2)$$

and $T_{ij}(r) \rightarrow 4\pi r \rho_j$ as $r \rightarrow \infty$, and table 3 shows the coordination numbers N_{ij} . The first peak in $T_{\text{AlO}}(r)$ at ~ 1.8 Å represents Al–O nearest neighbours. The model has 97% Al with fourfold coordination, i.e. $N_{\text{AlO}} = 4$. (The remaining 3% are fivefold-coordinated Al.) The average O–Al–O bond angle is tetrahedral, as shown in figure 3. The first peak in $T_{\text{CaO}}(r)$ at ~ 2.4 Å represents Ca–O nearest neighbours (discussed in the following paragraph). $T_{\text{OO}}(r)$ has a first peak at ~ 2.8 Å representing O coordinated to Al, i.e. O–Al–O configurations, and this is followed by a spread of correlations from 3.1–3.6 Å representing O coordinated to Ca,

Table 3. Distribution of coordination numbers N_{ij} for the model of $(\text{CaO})_{0.625}(\text{Al}_2\text{O}_3)_{0.375}$ glass (using cut-offs of 2.1 Å for Al–O and 3.0 Å for Ca–O). Values for the $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ crystal are shown in parentheses.

N (%)	N_{AlO}	N_{OAl}	N_{CaO}	N_{CaO_b}	$N_{\text{CaO}_{\text{nb}}}$	$N_{\text{O}_b\text{Ca}}$	$N_{\text{O}_{\text{nb}}\text{Ca}}$
0	—	1	—	1	3	1	—
1	—	31 (29)	—	13	14	33 (30)	—
2	—	63 (71)	—	21	27 (40)	55 (70)	5
3	—	5	—	22 (60)	25 (60)	11	65 (75)
4	97 (100)	—	—	23 (40)	23	—	28 (25)
5	3	—	19	13	6	—	2
6	—	—	50 (100)	7	2	—	—
7	—	—	26	1	—	—	—
8	—	—	5	—	—	—	—
Avg. N	4.0 (4.0)	1.7 (1.7)	6.2 (6.0)	3.3 (3.4)	2.8 (2.6)	1.8 (1.7)	3.3 (3.3)

i.e. O–Ca–O configurations. $T_{\text{AlAl}}(r)$ has a wide first peak at ~ 3.2 Å representing Al–Al nearest neighbours in the alumina network, which generally have Al–O–Al bond angles in the region 120° – 140° (see figure 3). Al–Ca and Ca–Ca correlations overlap and are significant in the region 3–4 Å.

The model has average Ca–O coordination $N_{\text{CaO}} = 6.2$. Table 3 shows a narrow distribution of Ca–O coordination numbers, with sixfold coordination being the most common. The O–Ca–O bond angle shown in figure 3 represents CaO_N polyhedra, and is peaked at $\sim 80^\circ$ with a shoulder at larger angles extending to 180° , as expected for predominantly distorted octahedral coordination. A pronounced peak at $\sim 70^\circ$ can be assigned to capped octahedra with $N_{\text{CaO}} = 7$. Oxygen atoms with two or more Al nearest neighbours have been classified as bridging oxygen, O_b ; otherwise, as non-bridging oxygen, O_{nb} . As shown in table 3, the model has average values of $N_{\text{CaO}_{\text{nb}}} = 2.8$ and $N_{\text{CaO}_b} = 3.3$, so Ca is typically coordinated to three O_{nb} and three O_b .

To describe the connectivity of the alumina network, each Al is classified as Q^n where n is the number of O_b coordinated to Al, i.e. $N_{\text{AlO}_b} = n$ and $N_{\text{AlO}_{\text{nb}}} = 4 - n$ (assuming all Al is fourfold coordinated). If all oxygen was coordinated to Al, the $x = 0.5$ composition of CaAl_2O_4 would have 100% Q^4 , and compositions with $x > 0.5$ would have polymerized tetrahedral alumina networks with average $\langle Q^n \rangle$ of $n < 4$. Table 4 shows that the model has a broad distribution of Q^n , with an average value of $n = 3.28$. Assuming all Al is fourfold coordinated, the average value of n can be predicted from the equivalence of $(\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x} \rightarrow \text{Ca}_x(\text{Al}_{2-2x}\text{O}_{3-2x}) \rightarrow \text{Ca}_{x/(2-2x)}\text{AlO}_{4-n/2}$, or

$$4 - \frac{n}{2} = \frac{3 - 2x}{2 - 2x}. \quad (3)$$

Solving this gives a value of $n = (5 - 6x)/(1 - x)$, which for $x = 0.625$ gives $n = 3.33$. This is in good agreement with the model. The polymerized alumina network contains rings of AlO_4 tetrahedra linked by O_b , and the distribution of ring sizes is a measure of network topology, as discussed in [27] for silicate glasses. The distribution of ring sizes for the model is shown in figure 4 (note that ring sizes > 14 are not shown).

The current modelling results can be compared with previous experimental results for $(\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}$ glasses with $x \sim 0.625$. The experimental results for R_{AlO} , N_{AlO} , R_{CaO} , and N_{CaO} are reported in table 5, and there is good agreement with the modelling results. The exceptions are the value of $N_{\text{AlO}} = 4.8$ reported for one neutron diffraction study [9], and values of $N_{\text{CaO}} \sim 4$ reported for two neutron diffraction studies [9, 10]. In fact, these

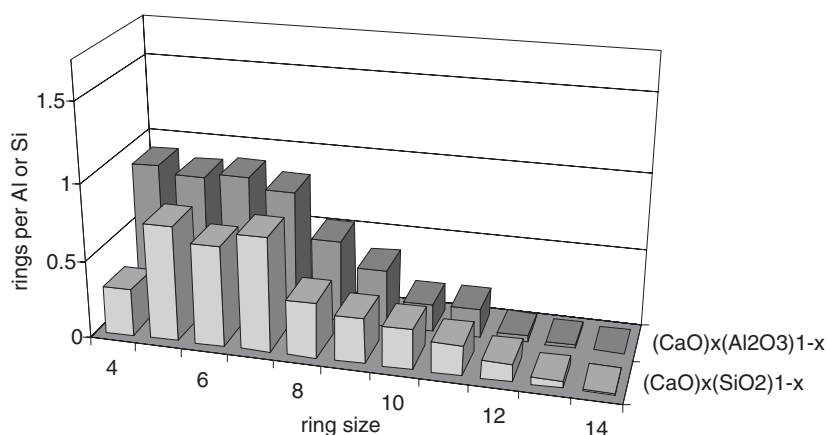


Figure 4. Ring size distribution in the alumina network for the model of $(\text{CaO})_{0.625}(\text{Al}_2\text{O}_3)_{0.375}$ glass. (Note that ring sizes >14 are not shown.)

Table 4. Alumina network polymerization for the model of $(\text{CaO})_{0.625}(\text{Al}_2\text{O}_3)_{0.375}$ glass, i.e. distribution of Q^n . (Not shown are 0.7% of Q^5 .)

Q^n	1	2	3	4
%	2.6	12.3	39.2	45.2

Table 5. Average nearest neighbour distances R and coordination numbers N for the model of $(\text{CaO})_{0.625}(\text{Al}_2\text{O}_3)_{0.375}$ glass with $x = 0.625$ and of $(\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}$ glasses from diffraction experiments. (Neutron diffraction results for N_{CaO} were reported to be too low [9, 10].)

Method	R_{AlO}	N_{AlO}	R_{CaO}	N_{CaO}
Neutron ($x = 0.64$) [9]	1.76	4.8	2.40	3.9
Neutron ($x = 0.62$) [10]	1.76	4.0	2.34	4.0
X-ray ($x = 0.63$) [8]	1.77	4.2	2.37	5.6
Model	1.77	4.0	2.40	6.2
Model (O_{nb} only)	1.75	0.8	2.37	2.8
Model (O_{b} only)	1.77	3.2	2.44	3.4

studies commented that the low values of $N_{\text{CaO}} \sim 4$ could arise because of additional Ca–O correlations at distances significantly larger than 2.4 \AA [9, 10], and these are present in the model (see figure 2). Figures 5 and 6 (respectively) show experimental x-ray [8, 9] and neutron [9, 10] diffraction structure factors $S(Q)$. The $S(Q)$ from the model have been calculated using

$$Q(S(Q) - 1) = \sum_{ij} w_{ij}(Q) \int (T_{ij}(r) - r\rho_{0j}) \sin(Qr) dr \quad (4)$$

where $w_{ij}(Q)$ is the weighting factor for scattering from correlations between elements i and j [29]. The model $S(Q)$, also shown in figures 5 and 6, are in good agreement with the experimental $S(Q)$.

A ^{27}Al NMR study [7] of several glasses with x from 0.55 to 0.75, including $x = 0.60$, concluded that in all of the glasses Al was 100% fourfold coordinated. It was observed that chemical shift δ increased with increasing x , but this could not be reliably interpreted in terms of polymerization. A ^{17}O NMR study [6] of a glass with $x = 0.62$ concluded that the proportion

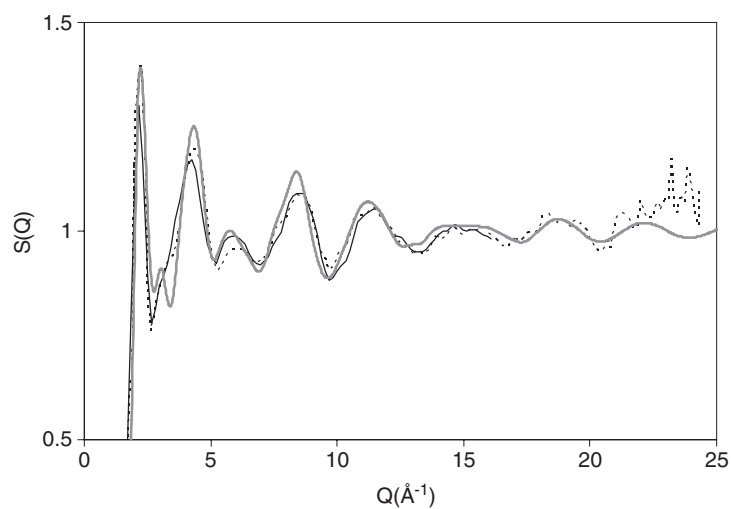


Figure 5. X-ray diffraction structure factors $S(Q)$ of $(\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}$ glass for the model with $x = 0.625$ (grey line) and from experiments with $x = 0.632$ (solid line) [8] and $x = 0.64$ (dotted line) [9].

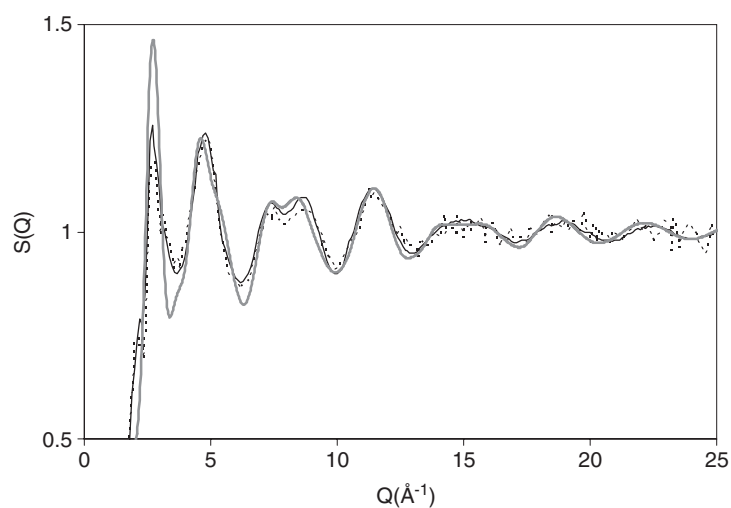


Figure 6. Neutron diffraction structure factors $S(Q)$ of $(\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}$ glass for the model with $x = 0.625$ (grey line) and from experiments with $x = 0.62$ (solid line) [10] and $x = 0.64$ (dotted line) [9].

of $f_{\text{O}_{\text{nb}}} = O_{\text{nb}}/(O_{\text{b}} + O_{\text{nb}})$ was $f_{\text{O}_{\text{nb}}} = 0.27$. This is related to $\langle Q^n \rangle$ because $N_{\text{AlO}_{\text{nb}}} = 4 - n$ and $f_{\text{O}_{\text{nb}}} = N_{\text{AlO}_{\text{nb}}}/(N_{\text{AlO}_{\text{nb}}} + N_{\text{AlO}_{\text{b}}}/2)$, and hence $n = 8(1 - f_{\text{O}_{\text{nb}}})/(2 - f_{\text{O}_{\text{nb}}})$. The experimental value of $f_{\text{O}_{\text{nb}}} = 0.27$ corresponds to an average $n = 3.38$, which is similar to the value of $n = 3.33$ predicted from equation (3), and is similar to the model value of $n = 3.28$ (both for $x = 0.625$).

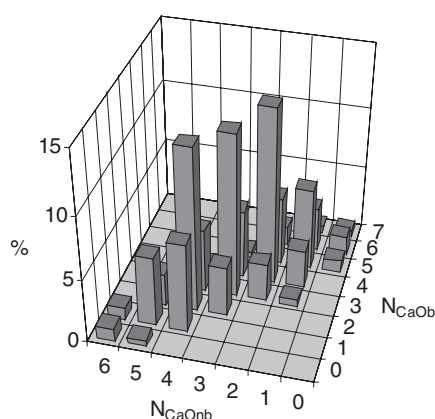


Figure 7. Distribution of Ca coordinations $N_{\text{CaO}} = N_{\text{CaO}_{\text{nb}}} + N_{\text{CaO}_{\text{b}}}$ in terms of $N_{\text{CaO}_{\text{nb}}}$ (x -axis) and $N_{\text{CaO}_{\text{b}}}$ (y -axis) for the model of $(\text{CaO})_{0.625}(\text{Al}_2\text{O}_3)_{0.375}$ glass.

4. Discussion

The model obtained in the current study provides a detailed picture of the atomic structure of $(\text{CaO})_{0.625}(\text{Al}_2\text{O}_3)_{0.375}$ glass, close to the eutectic. This glass contains a corner-shared tetrahedral alumina network, as expected. There is a small content (3%) of fivefold-coordinated Al. The one previously reported model of a $(\text{CaO})_{0.61}(\text{Al}_2\text{O}_3)_{0.39}$ glass also featured a small content (2%) of fivefold-coordinated Al [13]. (Note that the model in the current study has a number of time steps $\approx 8 \times$ greater, and a quench rate $40 \times$ slower, than for the previous model [13].) The results appear consistent with the reported neutron diffraction result of $N_{\text{AlO}} = 4.0$ for $x = 0.62$ [10], but not $N_{\text{AlO}} = 4.8$ for $x = 0.64$ [9], although this is likely to reflect the influence of the fabrication method as discussed in the introduction.

Oxygen is playing the expected role in the alumina network with expected proportions of O_{b} and O_{nb} (assuming all Al is fourfold coordinated). There is a small amount (5%) of triply bridging oxygen, i.e. OAl_3 configurations which give rise to Al-O-Al bond angles around 90° (see figure 3). These were also found in the one previous model of a $(\text{CaO})_{0.61}(\text{Al}_2\text{O}_3)_{0.39}$ glass [13], but are not found in the $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ or $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ crystals. The alumina network in the model of $(\text{CaO})_{0.625}(\text{Al}_2\text{O}_3)_{0.375}$ glass has network polymerization with average $n = 3.28$, close to the expected value of $n = 3.33$. Figure 4 shows that the ring size distribution in the alumina network is similar to that for a model of $(\text{CaO})_{0.3}(\text{SiO}_2)_{0.7}$ glass which has a similar network polymerization with average $n = 3.2$ [30]. Note that these correspond to approximately the same ratios of $x_{\text{Al}}:x_{\text{O}} = 0.43$ and $x_{\text{Si}}:x_{\text{O}} = 0.41$ (respectively).

Ca acts as a network modifier with an average coordination of $N_{\text{CaO}} = 6.2$. This is consistent with the observation that the Ca coordination in oxide crystals is usually 6 or higher [31]. Ca is approximately equally coordinated by O_{b} and O_{nb} with an average $N_{\text{CaO}_{\text{nb}}} = 2.8$ and $N_{\text{CaO}_{\text{b}}} = 3.3$ as shown in table 3. The current study presents for the first time (see figure 7) the distribution of $N_{\text{CaO}} = N_{\text{CaO}_{\text{nb}}} + N_{\text{CaO}_{\text{b}}}$ in terms of $N_{\text{CaO}_{\text{nb}}}$ (x -axis) and $N_{\text{CaO}_{\text{b}}}$ (y -axis). The most common combinations of $N_{\text{CaO}_{\text{b}}} + N_{\text{CaO}_{\text{nb}}}$ are equal to $4+2$, $3+3$, and $2+4$ (respectively). For comparison, figure 8 shows the distribution of N_{CaO} in $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ crystal.

It is informative to consider Ca bonding to O in terms of bond valence. For fourfold-coordinated Al and (typically) sixfold-coordinated Ca, the average bond valence of Al-O bonds will be $3/4 = 0.75$ and of Ca-O bonds will be $2/6 = 0.33$. O_{b} in $\text{Al-O}_{\text{b}}-\text{Al}$ configurations

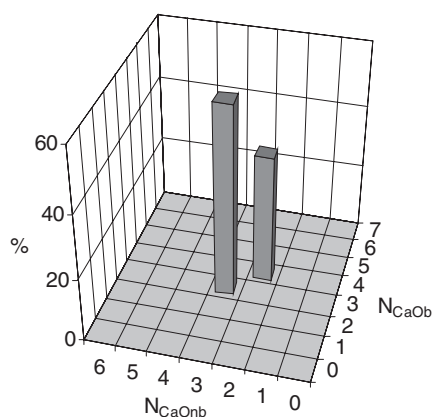


Figure 8. Distribution of Ca coordinations $N_{\text{CaO}} = N_{\text{CaO}_{\text{nb}}} + N_{\text{CaO}_{\text{b}}}$ in terms of $N_{\text{CaO}_{\text{nb}}}$ (x -axis) and $N_{\text{CaO}_{\text{b}}}$ (y -axis) for the $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ crystal ($x = 0.625$) [23].

would have a bond valence of 1.5, and could provide in addition 1.5 Ca–O_b bonds with bond valence $0.5/1.5 = 0.33$. Table 3 shows an average $N_{\text{O}_{\text{b}}\text{Ca}} = 1.8$ which implies an average O_b–Ca bond valence of $0.5/1.8 = 0.28$. In comparison, O_{nb} in Al–O_{nb} configurations would have a bond valence of 0.75, and could provide in addition four Ca–O_{nb} bonds with bond valence of $1.25/4 = 0.31$. Table 3 shows an average $N_{\text{O}_{\text{nb}}\text{Ca}} = 3.3$ which implies an average O_{nb}–Ca bond valence of $1.25/3.3 = 0.38$. Thus there is a tendency for Ca–O_{nb} bonds to be strengthened, and hence shorter, and for Ca–O_b bonds to be weakened, and hence longer, as seen in the $T_{ij}(r)$ shown in figure 2. The likely explanation for this is that it is geometrically difficult for every O_{nb} to be coordinated to one Al plus four Ca, and hence $N_{\text{O}_{\text{nb}}\text{Ca}} < 4$.

It is also informative to compare the local atomic environments of Al, O, and Ca in the model of $(\text{CaO})_{0.625}(\text{Al}_2\text{O}_3)_{0.375}$ glass with those in the $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ and the $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ crystals which are both close to the eutectic and have 100% tetrahedral Al. The $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ crystal has distributions of $N_{\text{O}_{\text{b}}\text{Ca}}$ equal to 1 and 2, and $N_{\text{O}_{\text{nb}}\text{Ca}}$ equal to 3 and 4, and has $N_{\text{CaO}_{\text{b}}} + N_{\text{CaO}_{\text{nb}}}$ equal to $4 + 2$ and $3 + 3$ (see table 3 and figure 8), which are all similar to those for the glass. In fact, a previous x-ray diffraction study which interpreted the glass data by comparison with crystalline models concluded that the short range order in the glass is similar to that in $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ crystal [8].

The final point of discussion concerns the Ca distribution. The average number of Ca–Ca nearest neighbours, N_{CaCa} , was calculated using a cut-off of 5.0 \AA corresponding to the minimum in $T_{\text{CaCa}}(r)$. The model of $(\text{CaO})_{0.625}(\text{Al}_2\text{O}_3)_{0.375}$ glass has average $N_{\text{CaCa}} = 7.0$. In comparison, the $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ crystal has $N_{\text{CaCa}} = 6$, and the $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ crystal has $N_{\text{CaCa}} = 4$. The average connectivity between two neighbouring CaO_N polyhedra was examined by calculating the numbers of oxygen which they share (values of 1, 2, and 3 correspond to corner, edge, and face sharing respectively). An average value of 1.50 was obtained for the glass. In comparison, the $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ crystal has mostly edge sharing. The Ca distribution was also described using the function $G_{\text{CaCa}}(r) = T_{\text{CaCa}}(r) - 4\pi r\rho_{\text{Ca}}$. Figure 9 shows that $G_{\text{CaCa}}(r)$ for the model of $(\text{CaO})_{0.625}(\text{Al}_2\text{O}_3)_{0.375}$ glass has a remarkable similarity to that for a model of $(\text{CaO})_{0.5}(\text{SiO}_2)_{0.5}$ glass [30], and is also similar to the experimental $G_{\text{CaCa}}(r)$ of $(\text{CaO})_{0.5}(\text{SiO}_2)_{0.5}$ glass obtained using neutron diffraction [32]. This can be attributed to the similar number densities of Ca, $\rho_{\text{Ca}} = 0.015 \text{ atm \AA}^{-3}$, in the two glasses. Note that this corresponds to similar ratios of $x_{\text{Ca}}:x_{\text{Al}} = 0.83$ and $x_{\text{Ca}}:x_{\text{Si}} = 1.0$ (respectively). Figure 1 shows that the Ca distribution in the glass does not have any easily identifiable medium

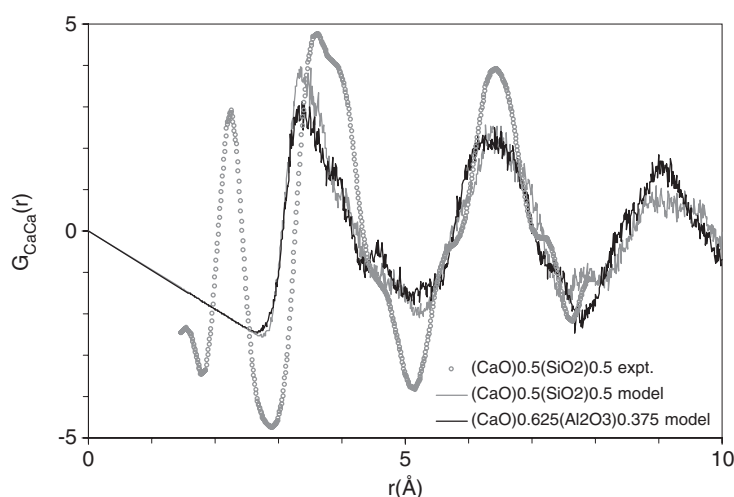


Figure 9. Ca–Ca distribution function $G_{\text{CaCa}}(r) = T_{\text{CaCa}}(r) - 4\pi r\rho_{\text{Ca}}$ for the model of $(\text{CaO})_{0.625}(\text{Al}_2\text{O}_3)_{0.375}$ glass, the model of $(\text{CaO})_{0.5}(\text{SiO}_2)_{0.5}$ glass [30], and neutron diffraction of $(\text{CaO})_{0.5}(\text{SiO}_2)_{0.5}$ glass [32]. (The peak at 2.3 Å in the neutron diffraction results was attributed as an artefact [32].)

range structure, such as Ca arranged in two-dimensional sheets as seen in the $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ crystal.

5. Conclusions

The current study has obtained an accurate and detailed model of the atomic structure of $(\text{CaO})_{0.625}(\text{Al}_2\text{O}_3)_{0.375}$ glass close to the eutectic. The glass consists of a tetrahedral alumina network with average $n = 3.3$. Ca acts as a network modifier with average coordination of 6.2. Previous neutron diffraction studies gave lower values of $N_{\text{CaO}} \sim 4$ but the discrepancy may be explained by the presence of additional Ca–O correlations at distances significantly larger than 2.4 Å. Ca is typically coordinated to three bridging oxygen (O_b) and three non-bridging oxygen (O_{nb}), with Ca– O_{nb} bonds noticeably shorter than the Ca– O_b bonds. A new method for analysing modifier cation coordination is presented, which specifically shows the distribution of Ca coordination $N_{\text{CaO}} = N_{\text{CaO}_b} + N_{\text{CaO}_{nb}}$ in terms of N_{CaO_b} and $N_{\text{CaO}_{nb}}$, the most common combinations being 4 + 2, 3 + 3, and 2 + 4 (respectively). O_b is most often coordinated to two Al plus two Ca, and O_{nb} is most often coordinated to one Al plus three Ca. The typical coordinations of Ca, O_b , and O_{nb} all have a noticeable similarity to those for the $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ crystal, and not the $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ crystal. The Ca–Ca distribution shows a remarkable similarity to that for $(\text{CaO})_{0.5}(\text{SiO}_2)_{0.5}$ glass, which is attributed to the equal atomic number densities of Ca in these two glasses. The Ca–Ca distribution does not show any identifiable medium range structure.

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